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WADC TECHNICAL REPORT 55-220

PART IV

ASTIA DOCUMENT No. 151180

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DISC

DEVELOPMENT OF FLUORO-SILICONE ELASTOMERS

BYRON H. WISE

PENINSULAR CHEMRESEARCH, INC.

Best Available Copy

APRIL 1958

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WRIGHT AIR DEVELOPMENT CENTER

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WADC TECHNICAL REPORT 55-220

PART IV

ASTIA DOCUMENT No. 151180

DEVELOPMENT OF FLUORO-SILICONE ELASTOMERS

BYRON H. WISE

PENINSULAR CHEMRESEARCH, INC.

APRIL 1958

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-3238
PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by Peninsular ChemResearch, Inc. under USAF Contract No. AF 33(616)-3238. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers". The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Dr. Christ Tamborski acting as project engineer.

This report covers work conducted from December 15, 1956 to December 15, 1957.

The help of Dr. Paul Tarrant, Mr. Van A. May and Dr. George B. Butler is acknowledged with appreciation.

ABSTRACT

Some promising fluoroalkylsilane monomers and polymers have been prepared for use as high temperature and aircraft fuel resistant elastomeric materials.

In addition to the halosilanes previously synthesized, the following new silanes were prepared:

Bis(trifluoropropyl)dichloro-
silane

(Chlorohexafluorocyclobutylethyl)-
methyldichlorosilane

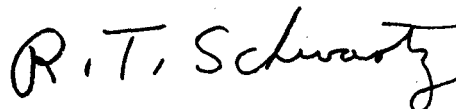
(2-Trifluoromethyltrifluoropropyl)-
methyldichlorosilane.

Polymerization of the cyclic polymers of (pentafluorobutyl)-methylsiloxane and (heptafluoropentyl)methylsiloxane was attempted, but resulted in oils of lower viscosity than desired. Polymerization of the cyclic polymers of (trifluoropropyl)methylsiloxane yielded high viscosity oils and in one case an elastic gum was formed.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

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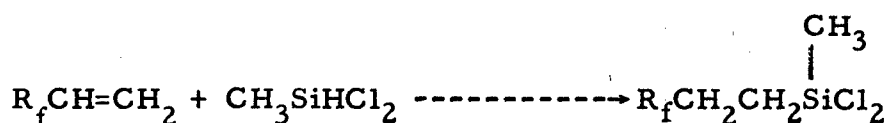
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INTRODUCTION

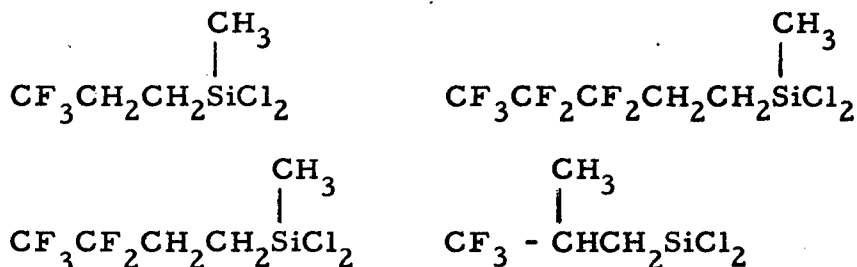
The work described in the ensuing report is part of the program to prepare elastomers whose properties make them applicable for use in advanced aircraft systems. These properties include retention of elasticity from -80°F. to $+500^{\circ}\text{F.}$ and resistance to swell in hydrocarbon fuels and ester hydraulic fluids. Because of the excellent thermal properties of the silicone rubbers and the insolubility of fluorocarbons in hydrocarbons, work was initiated to attach fluoroalkyl groups to halosilanes in hopes of combining the properties of thermal stability and resistance to fuel swell.

Previous reports of work performed under contract AF 33(600)-26593 and AF 33(616)-3238 describe the preparation of several (fluoroalkyl)-methylsilanes. The general method of preparation is shown:



where R_f is CF_3 - , C_2F_5 - and C_3F_7 - .

Silanes prepared by this method included:



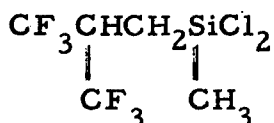
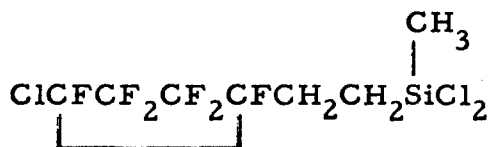
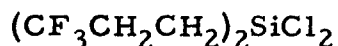
The preparation of the starting fluoroolefins has also been described previously.

The polymerization of the fluoroalkylsiloxanes by methods that have proven successful for the methyl siloxanes did not give elastomeric substances in this laboratory. However, the Dow-Corning Corporation has succeeded in polymerizing a sample of trifluoropropylmethyldichlorosilane made in this laboratory to an elastic gum. This elastomer has shown excellent thermal stability and solvent resistance. Rubbery gums were made in this laboratory from (trifluoropropyl)methyltrisiloxane by methods which are described in the experimental section of this report.

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WADC TR-55-220 Pt IV

In view of the excellent properties of trifluoropropyl(methyl) - silicone rubber, attempts to prepare an even superior elastomer were made by the synthesis of silanes having greater amounts of fluorine. Besides the pentafluorobutyl and heptafluoropentyl derivatives shown above, the following new monomers were prepared:



Attempts were also made to prepare fluids from the fluoro-alkylsilanes. Certain fluoroalkyldichlorosilanes were hydrolyzed to cyclic siloxanes which were converted under various conditions to higher molecular weight oils.

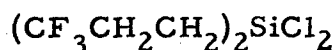
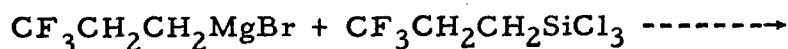
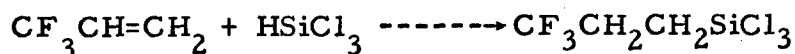
DISCUSSION

In the work performed during 1957, two objectives were set forth. First, it was decided to prepare new halosilane monomers containing greater amounts of fluorine than found in (trifluoropropyl)methyldichlorosilane yet having no more than four carbon atoms in a straight chain. Since it has been shown that silanes having a fluorine atom on any carbon atom closer to the silicon than the gamma position are hydrolytically unstable, it is obvious that the choice is very limited.

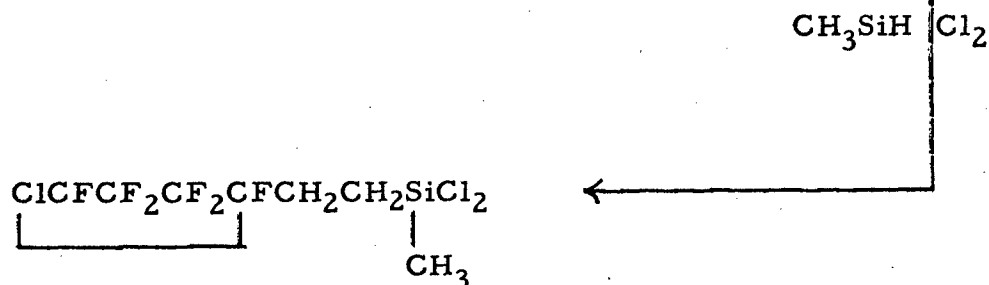
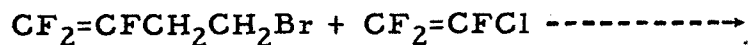
In addition to the synthesis of new monomers a secondary objective was the preparation of silicone oils from pentafluorobutyl and heptafluoropentyl derivatives.

The three new monomers prepared during the period have been enumerated in the introduction of this report. The methods of synthesis of these monomers follows:

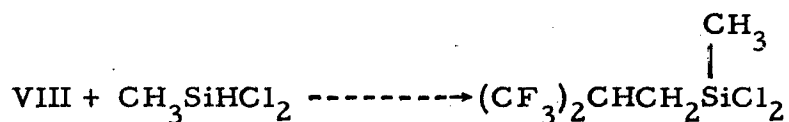
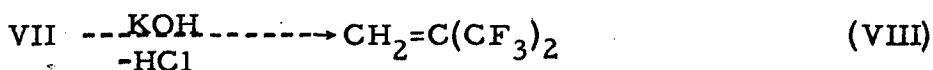
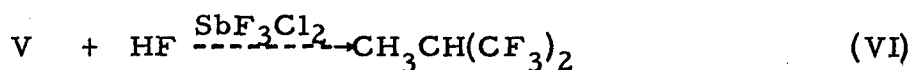
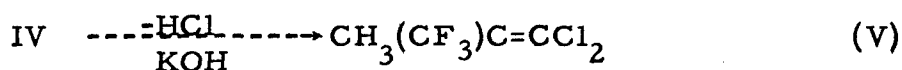
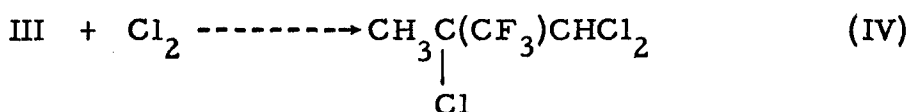
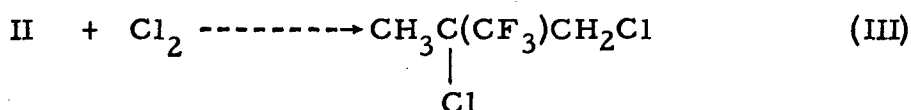
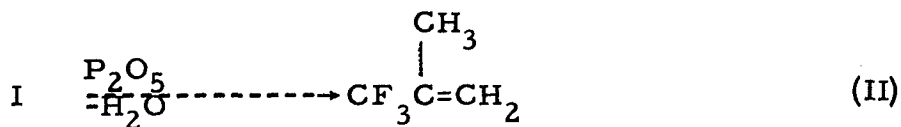
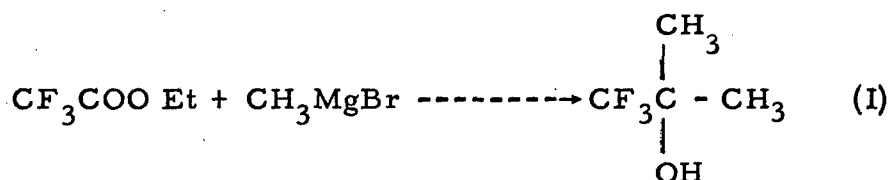
Bis-(trifluoropropyl)methyldichlorosilane



(Chlorohexafluorocyclobutylethyl)methyldichlorosilane



(2-Trifluoromethyltrifluoropropyl)methyldichlorosilane



The preparation of bis(trifluoropropyl)dichlorosilane by means of the Grignard reagent prepared from trifluoropropylbromide proceeded in the classic manner, but the reaction with trifluoropropyltrichlorosilane gave appreciable quantities of tris(trifluoropropyl)chlorosilane even when a large excess of the silane was used. No attempt has been made to polymerize the bis compound.

As is shown above vinylhexafluorochlorocyclobutane was readily prepared by adding chlorotrifluoroethylene to 1, 1, 2-trifluoro-4-bromobutene-1 and by dehydrohalogenating the resulting bromide. Attempts to establish the position of the chlorine atom are as yet inconclusive although a cyclic structure for this compound has been established. Addition of methyldichlorosilane to this olefin gave low yields of the desired silane.

The preparation of (2-trifluoromethyltrifluoropropyl)methyldichlorosilane involved a long and tedious synthesis from 2-trifluoromethylpropene. The steps are enumerated above. In addition to the length of the synthesis, the last two steps resulted in very low yields, so that from 1823 grams of 2-trifluoromethylpropene only 17 grams of 2-trifluoromethyltrifluoropropene was obtained.

Methyldichlorosilane was added to the 2-trifluoromethyltrifluoropropene to give the (2-trifluoromethyltrifluoropropyl)methyldichlorosilane in 60% yield.

The second phase of the work consisted of attempts to prepare viscous oils from (pentafluorobutyl)methylsiloxanes and (heptafluoropentyl)methylsiloxanes. Quantities of up to one kilogram of each of the dichlorosilanes were prepared and hydrolyzed by a modification of the procedure described previously. Using the modified hydrolytic procedure, nearly all the dichlorosilanes were converted to the cyclic trimers and tetramers. Attempts to polymerize the tetramers with KOH and hexamethyldisiloxane and with metallic potassium and trimethylchlorosilane did not result in an appreciable change in viscosity. Analysis showed that dehydrofluorination had occurred under the conditions used. Attempts to polymerize the cyclic trimers by using metallic potassium and end blocking with trimethylchlorosilane did result in increased viscosity indicating that some polymerization had taken place.

In view of the lack of success with (pentafluorobutyl)methylsiloxanes and (heptafluoropentyl)methylsiloxanes, attention was turned late in the year to preparing fluids from (trifluoropropyl)methylsiloxanes. Here again, metallic potassium was employed to open the ring and trimethylchlorosilane to endblock.

The cyclic trimer quickly polymerized to a very viscous oil while the tetramer showed more reluctance, but was converted to an oil of considerably higher viscosity than the tetramer. In this case, no dehydrofluorination was observed.

It is apparent that some polymerization took place using the cyclic trimers of all three silanes. It is also apparent that the proper conditions for polymerization to fluids of the proper viscosity have not yet been attained.

SUMMARY AND CONCLUSIONS

Four new fluorine containing silanes were prepared during the report period by the addition of methyldichlorosilane to fluoroolefins and by the Grignard reaction.

Hydrolysis of the monomers $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$ and $\text{C}_3\text{F}_7\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$ was carried out by an improved procedure to achieve good yields of the cyclic trimers and tetramers. Attempts to prepare fluids of high viscosity from these cyclics was essentially unsuccessful in the case of $[\text{C}_3\text{F}_7\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{O}]_{3,4}$ but met with some degree of success in the case of $[\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{O}]_{3,4}$. These fluids have been submitted to WADC for evaluation. The $[\text{C}_3\text{F}_7\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{O}]_{3,4}$ indicated hydrolytic instability under the alkaline conditions with the attendant splitting out of HF.

The most promising results were achieved in polymerizing $[\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{O}]_{3,4}$ cyclics. Potassium sand was used to open the ring and end blocking was done with trimethylchlorosilane. Although only a few experiments were made due to the lack of time and materials, it is evident that fluids of any viscosity can be made by this method.

Fluids prepared from siloxanes containing the $-\text{CF}_2-$ groups adjacent to $-\text{CH}_2-$ groups do not appear to be practical using alkaline catalysts due to their tendency to dehydrofluorinate.

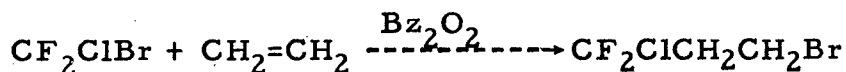
EXPERIMENTAL

I. The Preparation of Silane Monomers

A. The Preparation of 3,3-Difluoro-3-chloropropylmethyldi-chlorosilane

1. The Addition of Bromochlorodifluoromethane to

Ethylene



Bromochlorodifluoromethane (400 g., 2.4 moles), benzoyl peroxide (7 g.) and water (200 g.) were placed in a 1.4 liter stainless steel reaction vessel which had been cooled in a Dry-Ice-acetone bath. The reaction vessel was sealed using a block valve, rupture disc and gauge assembly, and ethylene (500 psi.) was added to the mixture. After mechanically rocking 4 hours at 90°C., the vessel was cooled to room temperature and the excess ethylene and unreacted CF_2ClBr were bled through a Dry-Ice trap, capturing the unreacted CF_2ClBr . The contents of the vessel were steam distilled, separated from the water and dried over anhydrous calcium chloride. Two experiments were carried out using this procedure. Fractionation of the combined products gave 155 g. (16.5% conversion) of the desired compound boiling at 95-105°C. A center fraction had the properties: b.p. 100°C., n_D^{25} 1.4115, d_4^{25} 1.6873. Anal. Calcd. for $\text{C}_3\text{H}_4\text{BrClF}_2$: ag eq., 96.72. Found: Ag eq., 96.46.

A large amount of 2:1 adduct (approximately 250 g.) was formed in these experiments. A third experiment was carried out under essentially the same conditions except that 800 g. (4.8 moles) of CF_2ClBr were used. Distillation in this instance gave only 62 g. (7.6% conversion) of product boiling at 98-103°C. However, some advantage was realized from this procedure in that only 81 g. of 2:1 adduct were formed.

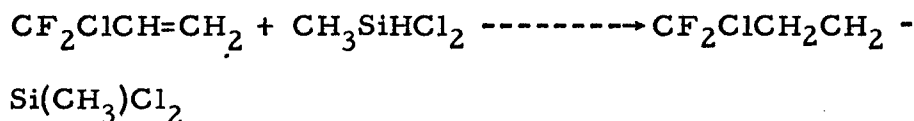
2. The Preparation of 3,3-Difluoro-3-chloropropene-1



Potassium hydroxide (168 g., 3.0 moles) in 500 ml. of ethanol was added dropwise, with stirring, to 217 g. (1.1 moles) of 1-bromo-3-chloro-3,3-difluoropropane. After the addition was complete, the mixture was refluxed, with stirring, for 2 hours, the gaseous product being collected

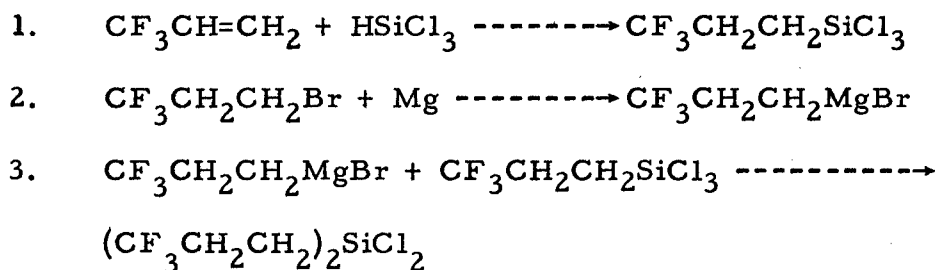
in a Dry-Ice-acetone-cooled trap. Fractional distillation yielded 65 g. of product, b. p. 16-16.5°C. (52%).

3. The Addition of Methylchlorosilane to 3,3-Difluoro-3-chloropropene-1



Methylchlorosilane (131 g., 1.14 moles) and $\text{CF}_2\text{Cl}-\text{CH}=\text{CH}_2$ (64.5 g., 0.57 mole) were placed in a 1.4 liter stainless steel autoclave which had been cooled in a Dry-Ice-acetone mixture. The vessel was sealed and rocked for 16 hours at 200°C., then cooled in ice-water and the gases vented. The contents of the vessel were fractionated to give 67.5 g. (30%) of product boiling at 65-70°C./40 mm. A center fraction had the following properties: b. p. 68°C./40 mm., n_D^{27} 1.4132, d_4^{25} 1.2969. Anal. Calcd. for $\text{C}_4\text{H}_7\text{Cl}_3\text{F}_2\text{Si}$: hydrolyzable Cl, 31.17%. Found: hydrolyzable Cl, 31.21%.

B. The Preparation of Bis-(3,3,3-trifluoropropyl)dichlorosilane

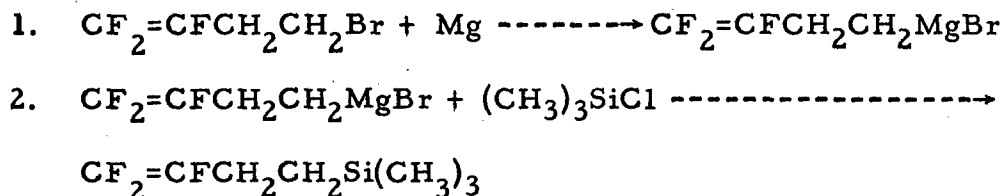


Trifluoropropene (264 g., 2.75 moles) was placed in a Dry-Ice-acetone-cooled 1.4 liter stainless steel autoclave with 660 g. (4.77 moles) of trichlorosilane and 0.5 g. platinum on charcoal catalyst. This was allowed to rock at 200°C. for 18 hours. Fractionation gave 499 g. (88%) of $\text{CF}_3\text{CH}_2\text{CH}_2\text{SiCl}_3$ boiling at 110-120°C.

A Grignard reagent was prepared from trifluoropropyl bromide (217 g., 1.3 moles) and magnesium (48 g., 2 atoms) in 1000 ml. of ethyl ether, using the usual apparatus, with nitrogen passing through the system at all times. The Mg/ether mixture was heated to reflux and approximately 5 ml. of methylmagnesium bromide was added to initiate the reaction. Trifluoropropyl bromide was added fast enough to maintain moderate refluxing. The mixture was refluxed for one hour after addition of the halide. The Grignard reagent was added dropwise, with the application of sufficient heat to maintain moderate refluxing,

to a stirred portion (499 g., 2.15 moles) of trifluoropropyltrichlorosilane. After addition, refluxing and stirring was continued for 5.5 hours. Fractional distillation yielded 45 g. of product boiling at 53-55°C./8 mm. Anal. Calcd. for $(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{SiCl}_2$: hydrolyzable Cl, 24.23%. Found: hydrolyzable Cl, 24.34%. Sixty grams of material was obtained boiling at 209-211°C. Anal. Calcd. for $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{SiCl}$: hydrolyzable Cl, 10.00%. Found: hydrolyzable Cl, 10.17%.

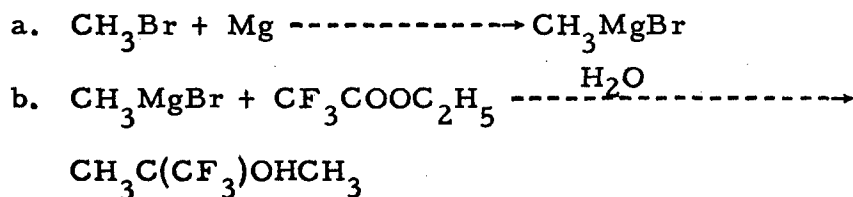
C. The Attempted Preparation of 3, 4, 4-Trifluoro-3-butenyl-trimethylsilane



Two hundred grams of 4-bromo-1, 1, 2-trifluorobutene-1 was added dropwise to a stirred slurry of 40 g. (1.66 moles) of magnesium in 450 ml. of ethyl ether, with nitrogen passing through the system at all times. A small amount (2-3 ml.) of methyl magnesium bromide was added to the refluxing slurry in order to initiate the reaction. After complete addition, the mixture was allowed to reflux for approximately 30 minutes. Chlorotrimethylsilane (125 g., 1.15 moles) was added to the mixture at such a rate as to insure constant refluxing, and stirring and refluxing were continued for an additional 4 hours after complete addition. Fractional distillation yielded only 33 g. of material boiling at 60-98°C., with no observed plateau.

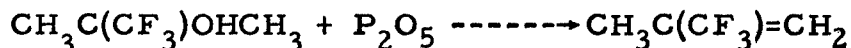
D. The Preparation of (3, 3, 3-Trifluoro-2-trifluoromethylpropyl)-methyldichlorosilane

1. The Preparation of Trifluoromethyldimethylcarbinol



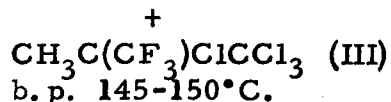
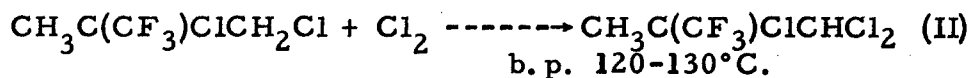
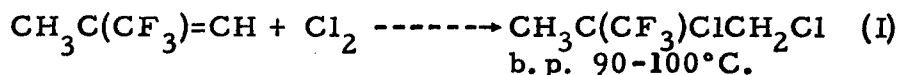
The Grignard reagent, methyl magnesium bromide, was prepared in typical manner by bubbling methyl bromide (712 g., 7.5 moles) through a stirred mixture of magnesium (182 g., 7.5 moles) in 2 liters of dry n-butyl ether. After addition of the methyl bromide, 497 g. (3.5 moles) of ethyl trifluoroacetate in 100 g. of n-butyl ether was added dropwise, with stirring. This was allowed to stand overnight, and was hydrolyzed with 5% hydrochloric acid. The aqueous layer was separated, extracted with n-butyl ether, and the combined ether solutions dried over Drierite. Nine runs were made using this procedure and fractionation in two batches yielded 2520 g. of the product boiling at 75-85°C., for an average yield of 53%.

2. The Preparation of 2-Trifluoromethylpropene



Trifluoromethyldimethylcarbinol (512 g., 4 moles) was added dropwise to 710 g. (5 moles) of phosphoric anhydride. The mixture was allowed to react about 48 hours. Fractionation of the material collected in the Dry-Ice-cooled receiver yielded 333 g. of material boiling at 3-9°C., (76%). Three additional runs were made, giving an additional 1490 g. of the olefin, for an overall average yield of 75%.

3. The Preparation of 1, 1, 2-Trichloro-2-trifluoromethylpropane



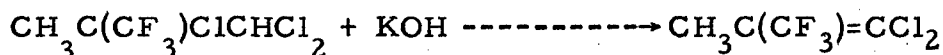
Chlorine (685 g.) was bubbled through a stirred portion (598 g., 5.4 moles) of 2-trifluoromethylpropene, maintaining the temperature in the reaction flask at -10 to -5°C. for the initial quarter of the reaction, then allowing the temperature to rise to 10°C. toward the end of the chlorine addition. The chlorinated product was washed with sodium bisulfite and with water and dried over calcium chloride. Fractionation gave 824 g. of (I), 90-100°C. (84%). Another run was made under similar conditions, giving 745 g. of (I), a 72% yield. Eight hundred twenty-four grams (4.6 moles) of (I) was chlorinated (309 g. of chlorine) using similar equipment, plus an ultra-violet light directed at the vapor phase in the reaction flask. The product

was washed and fractionated, giving 380 g. of forerun (I), 350 g. of (II) and about 130 g. of residue (III). A similar series of reactions yielded an additional 688 g. of (II).

A modification of this procedure was used in an attempt to combine two steps. In this variation, chlorine addition was continued up to a reaction flask temperature of 40-45°C., with an ultra-violet light being used above 20°C. This procedure gave higher (27%) percentage conversion to (II), much lower (47%) conversion to (I), and about five times the amount of residue (III).

A total of 1359 g. of $\text{CH}_3\text{C}(\text{CF}_3)\text{ClCHCl}_2$, b.p. 120-130°C., was obtained through the above procedures.

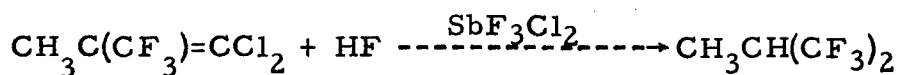
4. The Preparation of 1, 1-Dichloro-2-trifluoromethylpropene-1



Potassium hydroxide (252 g., 4.5 moles) in 800 ml. of ethanol was added to a stirred solution of 641 g. (3.0 moles) of 1, 1, 2-trichloro-2-trifluoromethylpropane in 100 ml. of ethanol at such a rate that the reaction temperature remained below 25°C. The reaction mixture was allowed to stand overnight, then filtered with suction, and the heavy, white precipitate washed several times with cold ethanol. The combined filtrates were rapidly distilled through a Claisen head to a reflux temperature of 88°C. The distillate was washed with cold water, and the organic layer separated and dried over calcium chloride.

Two additional runs were made and a total of 639 g. of product boiling at 86-94°C. was obtained for an average yield of 54%.

5. The Preparation of 1, 1, 1, 3, 3, 3-Hexafluoro-2-methylpropane

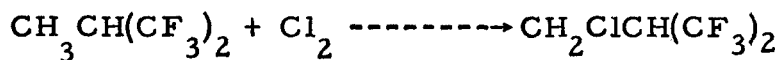


One hundred forty-two grams (2.0 moles) of chlorine and 234 g. (1.3 moles) of antimony trifluoride which had been oven-dried for 36 hours were loaded into a 1.4 liter autoclave cooled to -70°C. The autoclave was sealed and rocked at 50-60°C. for 2 hours. The excess chlorine was vented, the autoclave was again cooled, and hydrogen fluoride (53 g., 2.6 moles) and 1, 1-dichloro-2-trifluoromethylpropene-1 were added. The sealed autoclave was rocked for 5 hours at 55°C. and 7 hours at 135°C. The gases were vented at room temperature through two flasks containing respectively,

dry soda lime and concentrated sodium hydroxide solution and into a Dry-Ice-acetone-cooled trap in which 168 g. of crude olefin was collected.

Two additional runs were made. A total of 398 g. of the desired product boiling at 22-40°C. (95% boiling at 20-25°C.) was obtained for an average yield of 69%.

6. The Preparation of 1, 1, 1, 3, 3, 3-Hexafluoro-2-(chloromethyl)propane

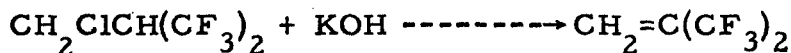


Three hundred grams (1.8 moles) of 1, 1, 1, 3, 3, 3-hexafluoro-2-methylpropane was chlorinated using the apparatus shown in Figure 1. Chlorine was introduced slowly at (A) while the organic material in the flask (B) was refluxed at a moderate rate from the Dry-Ice-acetone-cooled condenser (D). An ultraviolet lamp (Hanovia, 150 watt, with quartz burner) at (C) was directed at the vapor in the enclosure (E). The temperature in the flask (B) was maintained initially at 22°C. by limiting the rate of chlorine added, and was allowed to rise slowly to 46°C., adding chlorine at such a rate that the yellow color in the flask (B) did not become pronounced. On one or two occasions too much chlorine was added, reducing the temperature below the desired level.

The organic material was washed with sodium bisulfite and with water, dried over calcium chloride, and distilled, using a 12" silvered column and ice-water-cooled distilling head. Thirty grams was obtained boiling between 55-68°C., including a 15 g. center cut boiling at 57-60.3°C.

Another run was made in which the reaction temperature was not allowed to rise above 40°C., resulting in 25 g. of material (25%), b. p. 55-72°C.

7. The Preparation of 3, 3, 3-Trifluoromethyl-2-trifluoropropene



Potassium hydroxide (11.2 g., 0.20 mole) in 30 ml. of ethanol was added, with stirring, to 30 g. (0.15 mole) of 1, 1, 1, 3, 3, 3-hexafluoro-2-chloromethylpropane, at such a rate as to maintain moderate refluxing from an ice-water-cooled reflux condenser. The olefin formed was

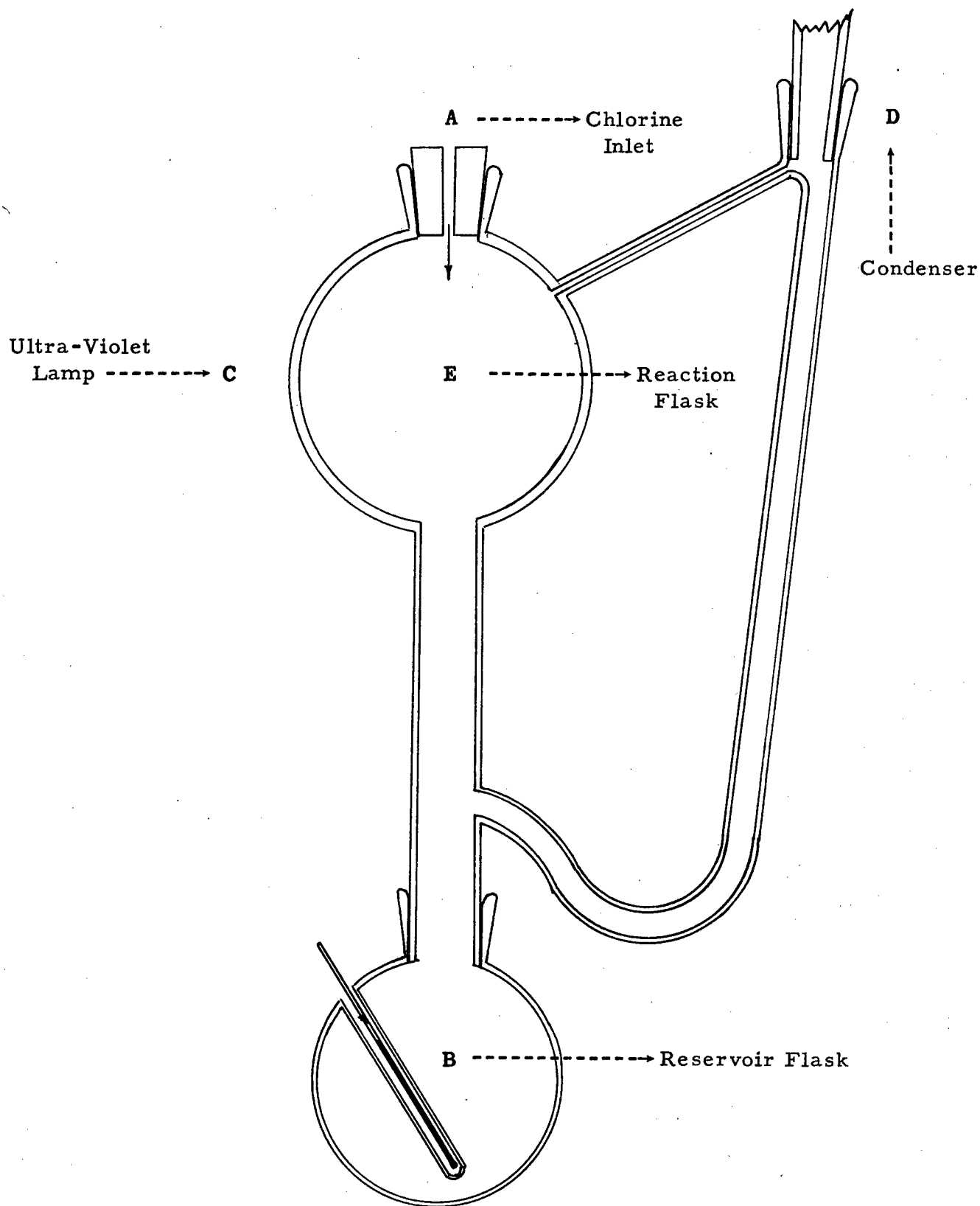
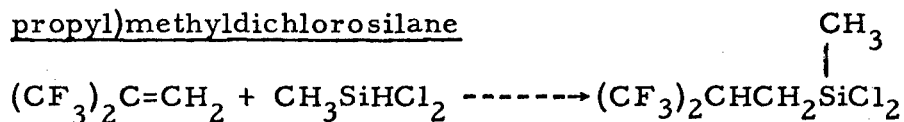


FIGURE 1. Chlorination Apparatus

allowed to pass through the condenser and was collected in a Dry-Ice acetone-cooled trap. Heat was applied to the reaction flask after completion of the addition to drive out any dissolved product. Distillation yielded 9 g. of material boiling at 20-23°C. (37%).

Another run was made giving 8 g. of product boiling at 20-23°C. (39%).

8. The Preparation of (2-Trifluoromethyl-3, 3, 3-trifluoropropyl)methyldichlorosilane

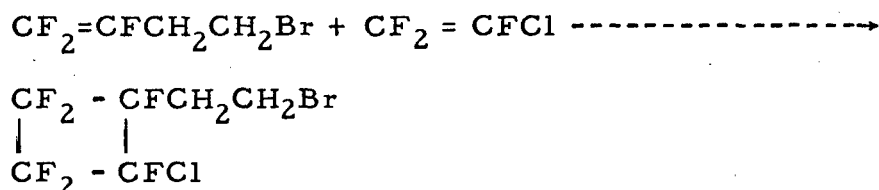


Seventeen grams of 2-trifluoromethyl-3, 3, 3-trifluoropropene (0.103 mole), 37 g. of methyldichlorosilane and 0.1 g. of 5% platinum on charcoal were charged into a 300 ml. autoclave and rocked for 24 hours at 225°C. The autoclave was cooled, the contents transferred to a 100 ml. flask and distilled.

After removing the excess methyldichlorosilane, the (2-trifluoromethyl-3, 3, 3-trifluoropropyl)methyldichlorosilane was distilled at 125-126°C. (760 mm.) Analysis: hydrolyzable Cl Calcd., 25.53. Found: 26.56.

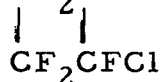
E. The Preparation of [2-(Chlorohexafluorocyclobutyl)ethyl] - methyldichlorosilane

1. The Preparation of 2-(Chlorohexafluorocyclobutyl) - ethyl bromide



A 1.4 liter stainless steel autoclave was cooled in Dry-Ice and acetone, charged with 4-bromo-1, 1, 2-trifluorobutene-1 and chlorotrifluoroethylene (233 g., 2.0 moles), and heated to 200°C. for 17 hours. The dark, heavy liquid was washed with water and dried over Drierite. Fractional distillation gave 100 g. of material boiling at 54-66°C., flat at 58°C., corresponding to the dimer, $(CF_2CFCF_2)_2$. Unreacted $CF_2=CFCH_2CH_2Br$ was collected at 93-98°C., amounting to approximately 100 g. The column was

removed and the contents distilled to a reflux temperature of 163°C. with a still temperature of 180°C., leaving approximately 100 g. of residue. This distillate was refractionated to give 80 g. of $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Br}$ boiling at 93-103°C. and 98 g. of material boiling at 145-150°C. corresponding to the desired product, $\text{CF}_2\text{CFCH}_2\text{CH}_2\text{Br}$ (16% conversion).

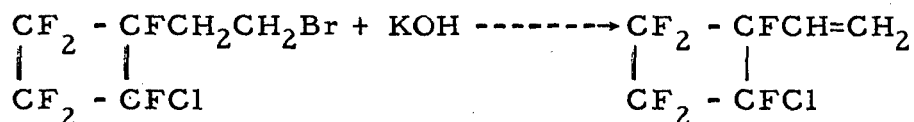


Another run was made using 300 g. (1.5 moles) of $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Br}$ and 506 g. (4.4 moles) of $\text{CF}_2=\text{CFCI}$, yielding 289 g. boiling at 42-144°C. and 108 g. of the desired product boiling at 144-151°C. (23%).

A third run, using a molar ratio of 1.9:4, yielded 159 g. of the desired product (28%).

2. The Dehydrobromination of 2-(Chlorohexafluorocyclobutyl)

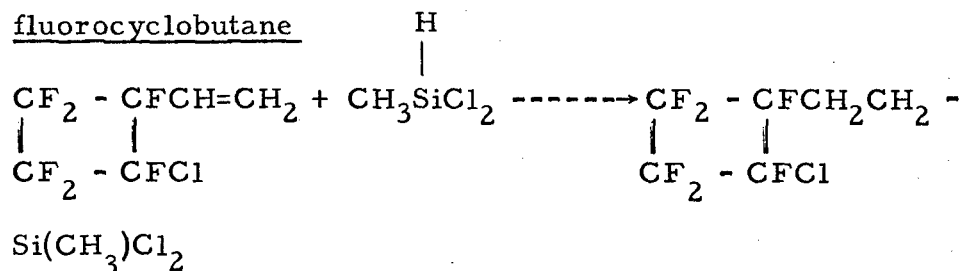
ethyl bromide



A solution of potassium hydroxide (47 g., 0.84 mole) in 175 ml. of 95% ethanol was added dropwise to 265 g. (0.87 mole) of $\text{C}_4\text{F}_6\text{-ClCH}_2\text{CH}_2\text{Br}$ in a 3-neck flask fitted with stirrer and reflux condenser. After addition was completed, the mixture was filtered to remove the precipitated potassium bromide and the filtrate heated to reflux for 0.5 hour and distilled to a head temperature of 78°C. Water was added and a lower layer was dried over calcium chloride. The product was fractionated through an 18" column with protruded packing to give 86 g. of material boiling at 83-84°C. (52%). A center fraction had the properties: b.p. 83.0°C., n_D^{22} 1.3468, d_4^{22} 1.4206. MR_D calcd. 32.60. MR_D found 33.71. Anal. calcd. for $\text{C}_6\text{H}_3\text{ClF}_6$: C, 32.10 H, 1.35 Cl, 15.71. Found: C 31.11, H 1.32, Cl 15.47.

3. The Addition of Methylchlorosilane to 2-Vinylchlorohexa-

fluorocyclobutane

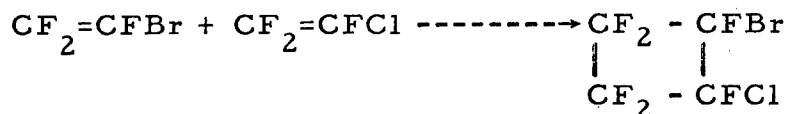


The olefin (89 g., 0.4 mole), methyldichlorosilane (215 g., 1.9 moles) and platinum (0.5 g.) were cooled in ice water and placed in an ice-water-cooled, 1.4 liter stainless steel autoclave. The mixture was allowed to rock for 12 hours at 200°C., and the adduct was distilled using a 27" silvered distilling column with a variable take-off head. The adduct was put under reduced pressure after the still temperature reached 245°C. The distillation was continued at 35 mm. until the residue began to decompose (approximately 300°C.). The distillate was redistilled and about 16 g. of material boiling at 170-182°C. was obtained.

A seven gram cut, b.p. 170-180°C., n_D^{24} 1.3910 was obtained. Anal. Calcd. for $C_7H_7Cl_3F_6Si$: hydrolyzable Cl, 20.94%. Found: 26.21%. Nine grams was obtained, b.p. 180-182°C., n_D^{24} 1.3909. Anal. Calcd. for $C_7H_7Cl_3F_6Si$: hydrolyzable Cl, 20.94%. Found: Cl, 26.21%.

F. The Attempted Proof of Structure of [2-(Chlorohexafluorocyclobutyl)ethyl]methyldichlorosilane

1. The Preparation of 1-Bromo-2-chloro-1, 2, 3, 3, 4, 4, hexafluorocyclobutane by the Addition of Bromotrifluoroethylene to Chlorotrifluoroethylene

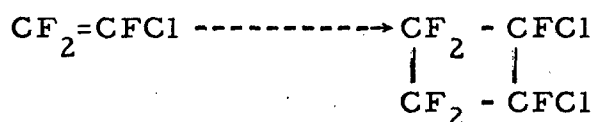


Bromotrifluoroethylene (197 g., 1.2 moles) and chlorotrifluoroethylene (300 g., 2.5 moles) were rocked at 200°C. during 15 hours in a 1.4 liter autoclave. The heavy, dark, viscous product was rapidly distilled, with two volumes of water, to a reflux temperature of 102°C. The heavy, water-white organic layer was dried over calcium chloride and the crude organic material was fractionated. Thirty-three grams of material were obtained, boiling at 68-95°C. There was no observed plateau during the distillation; the reflux temperature rose rapidly from 95°C. to 130°C.

Another run was made using equimolar quantities of the reactants and a reaction time of 6 hours. Fractionation yielded 62 g. of a material boiling at 77-80.5°C. (8.9%). Anal. Calcd. for C_4BrClF_6 : Ag equiv., 138.8. Found: Ag equiv., 145.4.

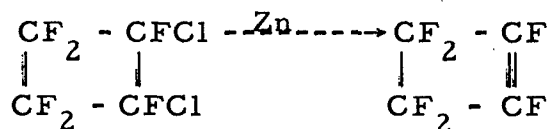
2. The Preparation of Hexafluorocyclobutene

a. The Preparation of 1, 2-Dichloro-1, 2, 3, 3, 4, 4-Hexafluorocyclobutane by the Dimerization of Chlorotrifluoroethylene



Four hundred forty-seven grams (3.8 moles) of chlorotrifluoroethylene was rocked at 200°C. during 20 hours in a 1.4 liter autoclave. Distillation of the product yielded 352 g. (79%) of material boiling at 60°C.

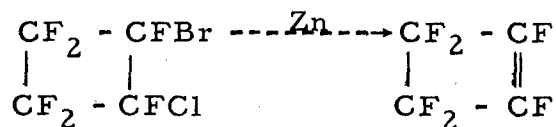
b. The Dechlorination of 1, 1-Dichloro-1, 2, 3, 3, 4, 4-hexafluorocyclobutane



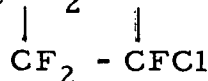
Five hundred seventy-three grams of (2.5 moles) 1, 2, 3, 3, 4, 4, -hexafluorocyclobutane was added to a stirred mixture of 237 g. of zinc metal and 1000 ml. ethanol sufficiently fast to maintain moderate refluxing. The product was collected in Dry Ice-acetone-cooled trap. Distillation gave 210 g. boiling at 3.5-7.5°C. (52%).

A second run gave 259 g. of crude material, which was not distilled, but was immediately used in the attempted preparation of 1-bromo-2-chloro-1, 2, 3, 3, 4, 4-hexafluorocyclobutane.

c. The Dehalogenation of 1-Bromo-2-chloro-1, 2, 3, 3, 4, 4-hexafluorocyclobutane



Thirty-three grams of material boiling between 68° and 95°C. (See F, 1 above), presumably containing $\text{CF}_2 - \text{CFBr}$ was treated



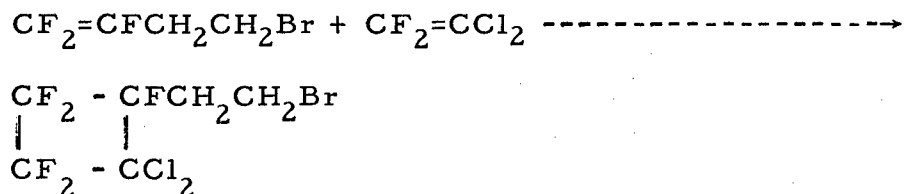
with zinc and alcohol. The material which was collected in a Dry-Ice-acetone cooled trap was fractionated, giving 2 g. of hexafluorocyclobutene, b. p. 4-7°C.

3. The Attempted Preparation of 1-Bromo-2-chloro-1, 2, 3, 3, 4, 4-Hexafluorocyclobutane by the Addition of Bromine to Hexafluorocyclobutene



One-half mole (35.5 g.) of chlorine and one-half mole (80 g.) of bromine were allowed to mix thoroughly at room temperature in a 1.4 liter autoclave to form BrCl. Hexafluorocyclobutene (359 g., 1.6 moles crude) was added to the autoclave at Dry-Ice temperature and the mixture was rocked for 8 hours at 100°C. Only a few drops of impure organic material was obtained other than recovered starting material.

G. The Addition of 1, 1-Dichloro-2, 2-difluoroethene to 4-bromo-1, 2, 2-trifluorobutene-1



One hundred eighty-nine grams (1.0 mole) of 4-bromo-1, 1, 2-trifluorobutene-1 and 266 g. (2.0 moles) of 1, 1-dichloro-2, 2-difluoroethene were placed in a 1.4 liter autoclave and rocked for 18 hours at 200°C.

Distillation with an 18" silvered column with a variable take-off head produced 24 g. of the product boiling at 167-179°C.

II. The Polymerization of Dialkylpolysiloxanes

A. Octamethylcyclotetrasiloxane

A mixture of 45 g. of octamethylcyclotetrasiloxane, 1 g. of hexamethyldisiloxane and 0.0075 g. of KOH were heated in an oil bath for 1 hour at 160°C. The mixture was cooled and proved to be so viscous that it would hardly

flow at room temperature. By varying the degree of end blocking, however, it was possible to prepare fluids having a viscosity of 3.00 to 12.9 poises.

III. The Modified Hydrolysis Procedure for (Heptafluoropentyl)methyldichlorosilane

Water (228 ml.) was placed in a 500 ml., three-neck flask and cooled in an ice bath to 2°C. A mixture of (heptafluoropentyl)methyldichlorosilane (280 g.) in 112 ml. of ethyl ether was added dropwise through a dropping funnel with stirring, keeping the temperature at about 5°C. The reaction mixture was allowed to stand overnight and the ether layer separated. The aqueous layer was extracted twice with 100 ml. portions of ether and dried over Drierite. The ether was stripped off and the residue distilled under reduced pressure. The following fractions were obtained:

<u>Fraction</u>	<u>B. P.</u>	<u>Yield</u>
I	118-125/2-3 mm.	56 g.
II	125-140/2-3 mm.	5 g.
III	140-150/2-3 mm.	98 g.
IV	150-210/2-3 mm.	34 g.
V	Residue	25 g.

Fraction I and II proved to be the cyclic trimer (n_D^{23} 1.3442) while fractions III and IV were the cyclic tetramer (n_D^{23} 1.3477). This modified procedure gave a much better yield of the cyclic trimer and tetramer than has been previously reported.

IV. The Polymerization of (Fluoroalkyl)methylpolysiloxanes

A. (Heptafluoropentyl)methyltetrasiloxane

Into a 100 ml., three-neck flask was charged 25 g. (heptafluoropentyl)methylcyclotetrasiloxane, 3 g. hexamethyldisiloxane and ca. 0.015 g. KOH.

The system was swept with dry nitrogen and heated to 160°C. for 2 hours. The mixture was allowed to cool, dissolved in isopropyl ether and washed with water to remove the potassium salts. The isopropyl ether was

removed by heating to 230°C. under vacuum. Viscosity increase was not appreciable.

An experiment using the same conditions but using the cyclic trimer instead of the tetramer gave no better results. A number of experiments using different catalysts were made, but they met with no more success than did that described above. Other catalysts employed were:

Boron Trifluoride - ethyl
etherate

Ferric Chloride - anhydrous

Zinc Chloride - anhydrous

Sulfuric Acid - fuming

Aluminum Chloride - anhydrous.

B. (Heptafluoropentyl)methylpolysiloxane

The pot residues from III. were combined to give 25 g. To this material was added 5 g. hexamethyldisiloxane and 0.015 g. of KOH. The reaction was run at 160°C. for 2 hours. The reaction mixture was cooled, taken up in isopropyl ether, washed with water and dried. The isopropyl ether was stripped under vacuum to a temperature of 200°C. The resulting fluid had a viscosity of 2.6 centistokes/25°C.

C. (Heptafluoropentyl)methyldichlorosilane with Potassium Sand

(Heptafluoropentyl)methylcyclotetrasiloxane (12 g.) and potassium sand (0.12 g.) were stirred in a micro flask under nitrogen for 48 hours. Some increase in viscosity was apparent. At the end of 48 hours 1 g. of trimethylchlorosilane was added. The fluid was filtered but no appreciable increase in viscosity was noted. The salts from the filtration were washed free of organic material and analyzed. The analysis showed these salts to contain 19.1% fluorine indicating the splitting out of HF from this type of compound.

D. (Trifluoropropyl)methylcyclotrisiloxane with Potassium Sand

(Trifluoropropyl)methylcyclotrisiloxane (9 g.) and potassium sand (0.8 g.) were stirred together in a micro-flask under nitrogen. The mixture rapidly became extremely viscous at which time 1 g. of trimethylchlorosilane was added. The resulting gum was taken up in chloroform and washed free of potassium salts. Upon removal of the solvent there was obtained a

highly viscous immobile fluid.

A similar experiment using (trifluoropropyl)methylcyclotetrasiloxane resulted in a fluid of lower viscosity.

PHYSICAL PROPERTIES OF NEW CHLOROSILANES

Compound	B. p.	n_D^{25}	d_4^{25}	Hydrolyzable Chlorine
$\text{CF}_2\text{ClCH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$	68°/40 mm.	1.4132 ^a	1.2969	31.21%
$(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{SiCl}_2$	53-55°/8 mm.	-	-	24.34%
$\text{ClCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{Si}(\text{CH}_3)\text{Cl}_2$	180-182°C.	1.3909 ^b	-	26.21%
$(\text{CF}_3)_2\text{CHCH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$	125-126°C.	-	-	26.56%

(a) Refractive index taken at 27°C.

(b) Refractive index taken at 24°C.